



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

Kunihiro ICHIMURA et al

SERIAL NO. 10/808,545

GROUP ART UNIT: 1712

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EXAMINER: Timothy J. Kugel

FOR: TRANSPARENT COLORING
COMPOSITION AND COLOR FILTER

DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF PATENTS & TRADEMARKS
WASHINGTON, D.C. 20231

SIR:

Now comes Kazuyuki HAYASHI, a citizen of Japan, and a resident of 34-43-20, Kawauchi 6-chome, Asaminami-ku, Hiroshima-shi, Hiroshima-ken, Japan, who declares and says that:

1. I graduated from Faculty of Engineering, Osaka Prefecture University in March, 1982; received a master's degree from the graduate school of the same university in March 1984.

2. I am currently employed by TODA KOGYO CORPORATION since 1984.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 09/940,866, and am a co-inventor of the U.S. Patents: No. 6,287,668, No. 6,294,242, No.

6,352,776, No. 6,416,864, No. 6,458,453, 6,531,211, and No. 6,544,647.

4. I have read the Office Action dated November 29, 2005, have understand the Examiner's rejection to the invention claimed in the above application, and have ascertained the following.

Experiment 1 (Example 1 of US Patent No. 6,596,071)

<Production of organic and inorganic composite pigments>

20 kg of titanium oxide particles (particle shape: granular shape; average particle diameter: 0.24 μm ; BET specific surface area value: 11.6 m^2/g ; L* value: 96.30; a* value: 0.78; b* value: -1.56; C* value: 1.74; hiding power: 1,490 cm^2/g ; light resistance (ΔE^* value): 6.86 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 96.21; a* value: -0.32; b* value: -0.80; C* value: 0.86; hiding power: 1,490 cm^2/g ; light resistance (ΔE^* value): 6.89 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.)) were deaggregated in 150 liters of pure water using a stirrer, and further passed through a "TK Pipeline Homomixer" (manufactured by TOKUSHU KIKI KOGYO CO., LTD.) three times, thereby obtaining a slurry containing the

titanium oxide particles.

Successively, the obtained slurry containing the titanium oxide particles was passed through a transverse-type sand grinder (tradename: "MIGHTY MILL MHG-1.5L", manufactured by INOUE SEISAKUSHO CO., LTD.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the titanium oxide particles were dispersed.

The titanium oxide particles in the obtained slurry, which remained on a sieve of 325 meshes (mesh size: 44 μm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a wet cake composed of the titanium oxide particles. The obtained wet cake composed of the titanium oxide particles was dried at 120°C. 10.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 294 N/cm (30 Kg/cm) for 30 minutes, thereby lightly deaggregating the particles.

Then, 100 g of methyltriethoxysilane "TSL8123" (tradename, produced by GE TOSHIBA SILICONE CO., LTD.) was mixed and diluted with 200 ml of ethanol to obtain a solution of methyltriethoxysilane. The methyltriethoxysilane solution was added to the deaggregated titanium oxide particles while operating the edge runner. The titanium oxide particles were continuously mixed and stirred at a linear load of 588 N/cm

(60 Kg/cm) and a stirring speed of 22 rpm for 30 minutes.

Next, 5 kg of organic pigments B-1 (kind: Pigment Blue (phthalocyanine-based pigments); particle shape: granular shape; average particle diameter: 0.06 μm ; BET specific surface area: 71.6 m^2/g ; hiding power: 630 cm^2/g ; L^* value: 17.70; a^* value: 9.72; b^* value: -23.44; light resistance (ΔE^* value): 10.84 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L^* value: 18.02; a^* value: 9.65; b^* value: -23.52; light resistance (ΔE^* value): 10.83 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) were added to the titanium oxide particles coated with methyltriethoxysilane for 10 minutes while operating the edge runner. Further, the obtained particles were continuously mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a stirring speed of 22 rpm for 20 minutes to form an organic pigment B-1 coat on the coating layer composed of methyltriethoxysilane.

Then, 50 g of a benzotriazole-based ultraviolet light-absorbing agent "TINUVIN 571" (tradename, produced by CIBA-GEIGY CO., LTD.) was added to the above-obtained composite particles for 10 minutes while operating the edge runner. Further, the resultant mixture was continuously mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a

stirring speed of 22 rpm for 30 minutes to adhere the benzotriazole-based ultraviolet light-absorbing agent onto the organic pigment B-1 coat. The thus obtained particles were heat-treated at 80°C for 60 minutes using a dryer, thereby obtaining organic and inorganic composite pigments.

Experiment 2 (Example 1 of US Patent No. 6,737,211)

<Production of colorant A>

440 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by GE TOSHIBA SILICONE CO., LTD.) was added to 11 kg of silica particles (particle shape: spherical shape; average particle diameter: 0.022 μm ; sphericity: 1.06; BET specific surface area value: 193.8 m^2/g ; specific gravity: 2.32; fluidity index: 55; L* value: 92.4; a* value: 0.2; b* value: 0.4; C* value: 0.4; hiding power: 10 cm^2/g (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 93.3; a* value: 0.14; b* value: 0.28; C* value: 0.3 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) while operating an edge runner, and the resultant mixture was mixed and stirred for 40 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm.

Then, 5.5 kg of organic pigments A (kind: Pigment Blue

(phthalocyanine-based pigments); particle shape: granular shape; average particle diameter: $0.06\ \mu\text{m}$; BET specific surface area value: $71.6\ \text{m}^2/\text{g}$; specific gravity: 1.65; L^* value: 17.7; a^* value: 9.7; b^* value: -23.4; C^* value: 25.4 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L^* value: 18.02; a^* value: 9.65; b^* value: -23.52; C^* value: 25.42 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) were added to the mixture for 20 minutes while operating the edge runner, and the resultant mixture was mixed and stirred for 60 minutes under a linear load of $588\ \text{N}/\text{cm}$ ($60\ \text{Kg}/\text{cm}$) at a stirring speed of 22 rpm, thereby adhering the organic pigments A onto the methyl hydrogen polysiloxane coating layer formed on the respective silica particles. The obtained particles were dried at 80°C for 60 minutes using a dryer, thereby obtaining a colorant A.

Experiment 3 (Example 1 of US Patent Application
publication No. 2002/0069790)

<Production of composite particles>

20 kg of titanium oxide particles (particle shape: granular shape; average particle size: $0.24\ \mu\text{m}$; BET specific surface area value: $11.6\ \text{m}^2/\text{g}$; L^* value: 94.15, a^* value: 1.06, b^* value: 2.22 and C^* value: 2.46 (when

measured by a portable spectrophotometer "COLOR-GUIDE 45/0" manufactured by BYK CHEMIE JAPAN CO., LTD.), L* value: 96.31, a* value: 1.06, b* value: -1.66 and C* value: 1.97); hiding power: 1,490 cm²/g; light resistance (ΔE^* value): 6.86 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 96.21; a* value: -0.32; b* value: -0.80; C* value: 0.86 light resistance (ΔE^* value): 6.89 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.)) were deaggregated in 150 liters of pure water using a stirrer, and further passed through a TK pipeline homomixer (manufactured by TOKUSHU KIKI KOGYO CO., LTD.) three times, thereby obtaining a slurry containing the titanium oxide particles.

Successively, the obtained slurry was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by INOUE SEISAKUSHO CO., LTD.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the titanium oxide particles were dispersed.

The titanium oxide particles in the obtained slurry, which remained on a sieve of 325 meshes (mesh size: 44 μ m) was 0 %. The slurry was filtered and washed with water, thereby obtaining a wet cake composed of the titanium oxide

particles. The obtained wet cake composed of the titanium oxide particles was dried at 120°C. 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.), and mixed and stirred at 294 N/cm (30 Kg/cm) for 30 minutes, thereby lightly deaggregating the particles.

Then, 110 g of methyltriethoxysilane "TSL8123" (tradename, produced by GE TOSHIBA SILICONE CO., LTD.) was mixed and diluted with 200 ml of ethanol to obtain a solution of methyltriethoxysilane. The methyltriethoxysilane solution was added to the deaggregated titanium oxide particles while operating the edge runner. The titanium oxide particles were continuously mixed and stirred at a linear load of 588 N/cm (60 Kg/cm) and a stirring speed of 22 rpm for 30 minutes.

Next, 1,100 g of organic pigment B-1 (kind: phthalocyanine-based pigment; particle shape: granular shape; average particle size: 0.06 μm ; BET specific surface area: 71.6 m^2/g ; hiding power: 240 cm^2/g ; L* value: 5.20, a* value: 9.14, and b* value: -21.84, (when measured by a portable spectrophotometer "COLOR-GUIDE 45/0", manufactured by BYK CHEMIE JAPAN CO., LTD.), L* value: 17.70, a* value: 9.72 and b* value: -23.44); light resistance (ΔE^* value): 10.84 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA

TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 18.02; a* value: 9.65; b* value: -23.52; light resistance (ΔE^* value): 10.83 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.)), was added to the titanium oxide particles coated with methyltriethoxysilane for 10 minutes while operating the edge runner. Further, the particles were continuously mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a stirring speed of 22 rpm for 20 minutes to form an organic pigment B-1 coat on the coating layer composed of methyltriethoxysilane. Then, the thus obtained coated particles were heat-treated at 105°C for 60 minutes by using a drier, thereby obtaining composite particles.

Experiment 4 (Example 1 of US Patent No. 6,623,557)

<Production of colorant>

280 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by GE TOSHIBA SILICONE CO., LTD.) was added to 7.0 kg of silica particles (core particles A; particle shape: spherical shape; average particle diameter: 0.022 μm ; sphericity: 1.06; BET specific surface area value: 193.8 m^2/g ; specific gravity: 2.32; L* value: 92.4; a* value: 0.2; b* value: 0.4; C* value: 0.4; hiding power: 10 cm^2/g (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES

MANUFACTURING CO., LTD.)(L* value: 93.3; a* value: 0.14; b* value: 0.28; C* value: 0.36 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) while operating an edge runner, and the resultant mixture was mixed and stirred for 30 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm.

Then, 7.0 kg of organic pigments A (kind: phthalocyanine-based pigments; particle shape: granular shape; average particle diameter: 0.06 μm ; BET specific surface area value: 71.6 m^2/g ; specific gravity: 1.65; hiding power: 630 cm^2/g ; light resistance (ΔE^* value): 10.8; L* value: 17.7; a* value: 9.7; b* value: -23.4; C* value: 25.4 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 18.02; a* value: 9.65; b* value: -23.52; C* value: 25.42 light resistance (ΔE^* value): 10.83 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) were added to the above-obtained mixture for 30 minutes while operating the edge runner, and the resultant mixture was mixed and stirred for 120 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm, thereby forming the organic pigments A coat onto the methyl hydrogen polysiloxane coating layer formed on the

respective silica particles. The obtained particles were dried at 80°C for 60 minutes using a dryer, thereby obtaining a colorant.

Experiment 5 (Example 1 of US Patent Application
publication No. 2003/0116758)

<Production of colorant G for color filter>

560 g of methyl hydrogen polysiloxane (trade name: "TSF484", produced by GE TOSHIBA SILICONE CO., LTD.) was added to 7.0 kg of silica (particle shape: spherical shape; average particle diameter: 0.022 μm ; BET specific surface area value: 193.8 m^2/g ; geometrical standard deviation value: 1.22; refractive index: 1.42; L* value: 92.4; a* value: 0.2; b* value: 0.4; C* value: 0.4; hiding power: 10 cm^2/g ; light resistance: 8.14 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 93.3; a* value: 0.14; b* value: 0.28; C* value: 0.30 light resistance (ΔE^* value): 8.06 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) while operating an edge runner, and the resultant mixture was mixed and stirred for 30 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm.

Then, 7.0 kg of organic pigments G-1 (kind:

phthalocyanine-based pigments; particle shape: granular shape; average particle diameter: $0.06\ \mu\text{m}$; BET specific surface area value: $60.5\ \text{m}^2/\text{g}$; L^* value: 21.83; a^* value: -18.31; b^* value: -7.36; hiding power: $210\ \text{cm}^2/\text{g}$; light resistance (ΔE^* value): 9.63 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L^* value: 24.16; a^* value: -19.21; b^* value: -3.14; light resistance (ΔE^* value): 9.65 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.)) were added to the above-obtained mixture for 30 minutes while operating the edge runner, and the resultant mixture was mixed and stirred for 120 minutes under a linear load of $588\ \text{N/cm}$ ($60\ \text{Kg/cm}$) at a stirring speed of 22 rpm, thereby forming the organic pigment G-1 coat onto the methyl hydrogen polysiloxane coating layer formed on the respective silica particles. The obtained particles were dried at 80°C for 60 minutes using a dryer, thereby obtaining a colorant G for color filter.

<Production of colorant R for color filter>

560 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by GE TOSHIBA SILICONE CO., LTD.) was added to 7.0 kg of silica particles (particle shape: spherical shape; average particle diameter: $0.022\ \mu\text{m}$; BET

specific surface area value: 193.8 m²/g; geometrical standard deviation value: 1.22; refractive index: 1.42; L* value: 92.4; a* value: 0.2; b* value: 0.4; C* value: 0.4; hiding power: 10 cm²/g; light resistance: 8.14 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 93.3; a* value: 0.14; b* value: 0.28; C* value: 0.30 light resistance (ΔE^* value): 8.06 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) while operating an edge runner, and the resultant mixture was mixed and stirred for 30 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm.

Then, 7.0 kg of organic pigments R-1 (kind: anthraquinone-based pigments; particle shape: granular shape; average particle diameter: 0.09 μ m; BET specific surface area value: 53.2 m²/g; L* value: 31.61; a* value: 63.66; b* value: 12.61; hiding power: 360 cm²/g; light resistance (ΔE^* value): 11.23 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 32.84; a* value: 60.18; b* value: 14.55; light resistance (ΔE^* value):11.18 (when measured by a spectrophotometric colorimeter "CM-3610d",manufactured by MINOLTA CO., LTD.)) were added to the above-obtained mixture for 30 minutes

while operating the edge runner, and the resultant mixture was mixed and stirred for 120 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm, thereby forming the organic pigment R-1 coat onto the methyl hydrogen polysiloxane coating layer formed on the respective silica particles. The obtained particles were dried at 80°C for 60 minutes using a dryer, thereby obtaining a colorant R for color filter.

<Production of colorant B for color filter>

560 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by GE TOSHIBA SILICONE CO., LTD.) was added to 7.0 kg of silica particles (particle shape: spherical shape; average particle diameter: 0.022 μm ; BET specific surface area value: 193.8 m^2/g ; geometrical standard deviation value: 1.22; refractive index: 1.42; L* value: 92.4; a* value: 0.2; b* value: 0.4; C* value: 0.4; hiding power: 10 cm^2/g ; light resistance: 8.14 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L* value: 93.3; a* value: 0.14; b* value: 0.28; C* value: 0.30 light resistance (ΔE^* value): 8.06 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.) while operating an edge runner, and the resultant mixture was mixed and

stirred for 30 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm.

Then, 7.0 kg of organic pigments B-1 (kind: phthalocyanine-based pigments; particle shape: granular shape; average particle diameter: 0.06 μm ; BET specific surface area value: 71.6 m^2/g ; L^* value: 17.70; a^* value: 9.72; b^* value: -23.44; hiding power: 240 cm^2/g ; light resistance (ΔE^* value): 10.84 (when measured by a multi-spectro-colour-meter "MSC-IS-2D", manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.)(L^* value: 18.02; a^* value: 9.65; b^* value: -23.52; light resistance (ΔE^* value): 10.83 (when measured by a spectrophotometric colorimeter "CM-3610d", manufactured by MINOLTA CO., LTD.)) were added to the above-obtained mixture for 30 minutes while operating the edge runner, and the resultant mixture was mixed and stirred for 120 minutes under a linear load of 588 N/cm (60 Kg/cm) at a stirring speed of 22 rpm, thereby forming the organic pigment B-1 coat onto the methyl hydrogen polysiloxane coating layer formed on the respective silica particles. The obtained particles were dried at 80°C for 60 minutes using a dryer, thereby obtaining a colorant B for color filter.

REFERENCE EXPERIMENTS

<Transparent coloring composition>

Each of the products obtained in Experiments 1 to 5, propylene glycol monomethyl ether acetate (PGMA) and a dispersant (basic comb-shaped polymer) were kneaded together at the following mixing ratio using a triple roll mill.

Product	100.0 parts by weight
Cyclohexanone	50.0 parts by weight
Dispersant (basic comb-shaped polymer; tradename: "Solsperse 24000" produced by Abicia Co., Ltd.)	20.0 parts by weight

The obtained kneaded material was mixed with 230.0 parts by weight of propylene glycol monomethyl ether acetate (PGMA), and the resultant mixture was dispersed using a beads mill, thereby obtaining a transparent coloring composition, respectively.

The properties in the particles were measured by the following methods.

(1) The average particle diameter of primary particles of the respective particles was expressed by an average value of particle diameters of 350 particles observed on a micrograph.

(2) The particle size distribution of the primary

particles was expressed by the geometrical standard deviation value obtained by the following method. That is, the particle sizes were measured from the above magnified micrograph. The actual particle sizes and the number of the particles were obtained from the calculation on the basis of the measured values. On a logarithmic normal probability paper, the particle sizes were plotted at regular intervals on the abscissa-axis and the accumulative number of particles (under integration sieve) belonging to each interval of the particle sizes were plotted by percentage on the ordinate-axis by a statistical technique. The particle sizes corresponding to the number of particles of 50% and 84.13%, respectively, were read from the graph, and the geometrical standard deviation was obtained from the following formula:

$$\text{Geometrical standard deviation} = \frac{\{\text{particle size corresponding to 84.13\% under integration sieve}\}}{\{\text{particle size (geometrical average diameter) corresponding to 50\% under integration sieve}\}}$$

The more the geometrical standard deviation is close to 1, the more excellent the particle size distribution of the primary particles.

(3) The specific surface area was expressed by the value measured by a BET method.

(4) The volume average particle diameter (D_{p50}) and the volume maximum particle diameter (D_{p99}) representing the conditions of behavior particles of the fine white inorganic particles and organic-inorganic composite pigment were measured as follows. That is, the sample particles were previously passed through a 60 mesh sieve (opening size: 250 μm), and then dried at 80°C for 3 hours using a drier. Thereafter, the respective parameters (D_{p50}) and (D_{p99}) of the sample particles were measured under a dispersion pressure of 0.1 MPa (1 bar) using a dry dispersion unit including a laser diffraction-type particle size distribution measuring device "Model HELOS LA/KA" (manufactured by Sympatec Co., Ltd.). Meanwhile, the behavior particles mean secondary particles formed by agglomeration of the primary particles.

(5) The degree of desorption of the organic pigment from the organic-inorganic composite pigment was visually observed and evaluated by the following method, and the observation results were classified into the following five ranks. The Rank 5 represents that the amount of the organic pigment desorbed from the surface of the organic-inorganic composite pigment was smallest.

That is, 2 g of the particles to be measured and 20 ml of ethanol were placed in a 50-ml conical flask and then

subjected to ultrasonic dispersion for 60 minutes. Thereafter, the obtained dispersion was centrifuged at a rotating speed of 10,000 rpm for 15 minutes to separate the particles from the solvent. The obtained particles were dried at 80°C for one hour, and the micrograph ($\times 50,000$) thereof was visually observed to count the number of the desorbed and re-aggregated organic pigment particles present in a visual field of the micrograph. The micrograph was compared with a micrograph ($\times 50,000$) of a physical mixture obtained by simply mixing the fine white inorganic particles with the organic pigment. The results are classified into the following five ranks.

Rank 1: Number of desorbed and re-aggregated particles was substantially the same as that in the physical mixture;

Rank 2: 30 to 49 desorbed and re-aggregated particles per 100 particles of the organic and inorganic composite pigment;

Rank 3: 10 to 29 desorbed and re-aggregated particles per 100 particles of the organic and inorganic composite pigment;

Rank 4: 5 to 9 desorbed and re-aggregated particles per

100 particles of the organic and inorganic composite pigment; and

Rank 5: 0 to 4 desorbed and re-aggregated particles per

100 particles of the organic and inorganic composite pigment.

(6) The hues of the fine white inorganic particles, organic pigment, and organic-inorganic composite pigment, were measured by the following method.

That is, 0.5 g of each sample and 0.5 ml of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately kneaded to form a paint. The obtained paint was applied onto a clear base film by using a 150 μm (6 mil) applicator to produce a coating film piece (having a coating film thickness of about 30 μm). The thus obtained coating film piece was placed on a standard white back plate and measured by a spectrophotometric colorimeter "CM-3610d" (manufactured by MINOLTA CO., LTD.) to determine color specification values thereof according to JIS Z 8929. Meanwhile, the C^* value representing chroma is calculated according to the following formula:

$$C^* = ((a^*)^2 + (b^*)^2)^{1/2}$$

(7) The tinting strength of the organic-inorganic composite pigment was measured by the following method.

That is, a primary color enamel and a vehicle enamel

prepared by the below-mentioned methods were respectively applied on a clear base film by using a 150 μm (6 mil) applicator to produce coating film pieces. The thus obtained coating film pieces were placed on a standard white back plate, and the L^* values thereof were measured by a spectrophotometric colorimeter "CM-3610d" (manufactured by MINOLTA CO., LTD.). The difference between the obtained L^* values was represented by a ΔL^* value.

Next, a control sample for the organic-inorganic composite pigment was prepared by simply mixing the organic pigment with the fine white inorganic particles at the same mixing ratio as used upon the production of the organic-inorganic composite pigment. Using the thus prepared mixed particles as a control sample, the same procedure as defined above was conducted to prepare an primary color enamel and a vehicle enamel, from respective coating film pieces and then measure L^* values thereof. The difference between the L^* values was represented by a ΔL_s^* value.

From the obtained ΔL^* value of the organic-inorganic composite pigment and ΔL_s^* value of the control sample, the tinting strength (%) was calculated according to the following formula:

$$\text{Tinting strength (\%)} = 100 + \{(\Delta L_s^* - \Delta L^*) \times 10\}$$

Preparation of primary color enamel:

10 g of the above sample particles, 16 g of an amino alkyd resin and 6 g of a thinner were blended with each other. The resultant mixture was added together with 90 g of 3mm ϕ glass beads into a 140-ml glass bottle, and then mixed and dispersed for 45 minutes by a paint shaker. The obtained mixture was mixed with 50 g of an additional amino alkyd resin, and further dispersed for 5 minutes by a paint shaker, thereby obtaining a primary color enamel.

Preparation of vehicle enamel:

12 g of the above-prepared primary color enamel and 40 g of Amirac White (titanium dioxide-dispersed amino alkyd resin) were blended with each other, and the resultant mixture was mixed and dispersed for 15 minutes by a paint shaker, thereby preparing a vehicle enamel.

(8) The photofatigue resistances of the fine white inorganic particles, organic pigment, and organic-inorganic composite pigment were measured by the following method.

That is, the primary color enamel prepared above for measuring the tinting strength was applied onto a glass plate (0.8 mm \times 70 mm \times 150 mm) and dried to form a coating film having a thickness of 150 μ m. One half of the thus prepared coating film piece was covered with a metal foil, and an ultraviolet light was continuously irradiated over the coating film piece at an intensity of 100 mW/cm² for 6

hours using "EYE SUPER UV TESTER SUV-W13" (manufactured by IWASAKI DENKI CO., LTD.). Then, the hue values (L^* , a^* and b^* values) of the metal foil-covered UV-unirradiated portion and the UV-irradiated portion of the coating film piece were respectively measured. On the basis of the measured value of the UV-unirradiated portion as a standard value, the ΔE^* value was calculated from differences between the measured hue values of the metal foil-covered UV-unirradiated portion and the UV-irradiated portion according to the following formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

wherein ΔL^* represents the difference between L^* values of the UV-unirradiated and UV-irradiated portions; Δa^* represents the difference between a^* values of the UV-unirradiated and UV-irradiated portions; and Δb^* represents the difference between b^* values of the UV-unirradiated and UV-irradiated portions.

(9) The viscosity of the transparent coloring composition was expressed by the value obtained by measuring the viscosity of the resultant composition at 25°C and a shear rate (D) of 1.92 sec^{-1} using "E-type Viscometer EMD-R" (manufactured by Tokyo Keiki Co., Ltd.).

(10) The dispersion average particle diameter (Dd_{50}), the dispersion particle diameter (Dd_{84}) and the dispersion

maximum particle diameter (Dd_{99}) of the organic-inorganic composite pigment contained in the transparent coloring composition were measured by a dynamic light scattering method using a concentrated particle size analyzer "FPAR-1000" (manufactured by Otsuka Denshi Co., Ltd.). Meanwhile, the geometrical standard deviation (Dd_{84}/Dd_{50}) was expressed by the value calculated according to the following formula:

$$\begin{aligned} &\text{Geometrical standard deviation } (Dd_{84}/Dd_{50}) = \\ &\{\text{particle size } (Dd_{84}) \text{ corresponding to 84.13\% under} \\ &\text{integration sieve}\} / \{\text{particle size } (Dd_{50}) \text{ corresponding to} \\ &50\% \text{ under integration sieve}\} \end{aligned}$$

The more the geometrical standard deviation value (Dd_{84}/Dd_{50}) is close to 1, the more excellent the particle size distribution of the behavior particles in the transparent coloring composition.

(11) The specific absorptivity values of the respective transparent coloring compositions were measured as follows. That is, the respective transparent coloring compositions were diluted 1,000 times with propylene glycol monomethyl ether acetate (PGMA). Using the thus prepared diluted solutions, the absorptivity coefficient at a wavelength of 550 nm in the case of the red-based coloring composition, the absorptivity coefficient at a wavelength of 650 nm in the case of the green-based coloring

composition and the absorptivity coefficient at a wavelength of 610 nm in the case of the blue-based coloring composition were respectively measured using a self-recording photoelectric spectrophotometer "UV-2100" (manufactured by SHIMADZU SEISAKUSHO CO., LTD.). The specific absorptivity of the respective transparent coloring compositions was expressed by the value calculated according to the following formula:

$$\varepsilon_w = \varepsilon_h / \varepsilon_0$$

wherein ε_w represents a specific absorptivity; ε_h represents an absorptivity coefficient per unit weight of the organic pigment contained in each organic-inorganic composite pigment; and ε_0 represents an absorptivity coefficient per unit weight of the organic pigment used as a raw material of each organic-inorganic composite pigment.

The larger the specific absorptivity value, the higher the tinting effect of the organic pigment coated on the fine white inorganic particles.

(12) The light transmittances of the transparent coloring compositions according to the first and second aspects of the present invention were measured as follows. That is, the respective transparent coloring compositions were diluted such that a concentration of the organic pigment contained therein was 0.0078% by weight, and then

filled in a quartz cell. Using the thus prepared diluted solutions each filled in the quartz cell, the light transmittances at wavelengths of 620 nm and 550 nm in the case of the red-based transparent coloring composition, the light transmittances at wavelengths of 530 nm and 650 nm in the case of the green-based transparent coloring composition and the light transmittances at wavelengths of 460 nm and 610 nm in the case of the blue-based transparent coloring composition, were respectively measured using a self-recording photoelectric spectrophotometer "UV-2100" (manufactured by SHIMADZU SEISAKUSHO CO., LTD.).

The results are shown in the Table 1.

Table 1

Examples	Properties of organic and inorganic composite pigment		
	Average particle diameter of primary particles (nm)	Geometrical standard deviation (-)	BET specific surface area value (m ² /g)
Experiment 1	240	1.41	12.8
Experiment 2	23	1.22	176.4
Experiment 3	240	1.40	13.8
Experiment 4	26	1.23	128.1
Experiment 5 (Green)	26	1.23	124.6
Experiment 5 (Red)	26	1.23	119.4
Experiment 5 (Blue)	26	1.23	128.3

Table 1 (continued)

Examples	Properties of organic and inorganic composite pigment	
	Volume average particle diameter (Dp ₅₀) (μm)	Volume maximum particle diameter (Dp ₉₉) (μm)
Experiment 1	7.15	20.41
Experiment 2	5.66	12.62
Experiment 3	7.18	20.59
Experiment 4	5.63	12.58
Experiment 5 (Green)	5.69	12.72
Experiment 5 (Red)	5.70	12.79
Experiment 5 (Blue)	5.67	12.75

Table 1 (continued)

Examples	Properties of organic and inorganic composite pigment		
	Hue		
	L* value (-)	a* value (-)	b* value (-)
Experiment 1	31.27	6.85	-19.05
Experiment 2	49.14	10.12	-20.89
Experiment 3	63.29	1.14	-30.71
Experiment 4	21.30	9.43	-21.02
Experiment 5 (Green)	24.81	-17.19	-7.90
Experiment 5 (Red)	33.97	59.88	11.86
Experiment 5 (Blue)	19.04	8.76	-21.14

Table 1 (continued)

Examples	Properties of organic and inorganic composite pigment		
	Tinting strength (%)	Photofatigue resistance (ΔE^* value) (-)	Desorption degree of organic pigment (-)
Experiment 1	136	1.31	5
Experiment 2	131	1.72	5
Experiment 3	138	2.49	5
Experiment 4	158	1.64	5
Experiment 5 (Green)	155	1.59	5
Experiment 5 (Red)	151	1.95	5
Experiment 5 (Blue)	150	1.49	5

Table 2

Examples	Properties of transparent coloring composition (I)		
	Viscosity (mPa·s)	Dispersion average particle diameter (Dd ₅₀) (nm)	Dispersion particle diameter (Dd ₈₄) (nm)
Experiment 1	950	582	2188
Experiment 2	80.1	401	1150
Experiment 3	963	613	2219
Experiment 4	77.4	397	1121
Experiment 5 (Green)	60.8	338	862
Experiment 5 (Red)	57.2	365	946
Experiment 5 (Blue)	72.9	341	887

Table 2 (continued)

Examples	Properties of transparent coloring composition (I)	
	Dispersion maximum particle diameter (Dd ₉₉) (nm)	Geometrical standard deviation (Dd ₈₄ /Dd ₅₀) (-)
Experiment 1	2675	3.76
Experiment 2	1261	2.86
Experiment 3	2829	3.62
Experiment 4	1287	2.82
Experiment 5 (Green)	1194	2.55
Experiment 5 (Red)	1224	2.59
Experiment 5 (Blue)	1166	2.60

Table 2 (continued)

Examples	Properties of transparent coloring composition (I)			
	Transmittance (R)		Transmittance (G)	
	620 nm (%)	550 nm (%)	530 nm (%)	650 nm (%)
Experiment 1	---	---	---	---
Experiment 2	---	---	---	---
Experiment 3	---	---	---	---
Experiment 4	---	---	---	---
Experiment 5 (Green)	---	---	68.8	1.5
Experiment 5 (Red)	63.8	3.1	---	---
Experiment 5 (Blue)	---	---	---	---

Table 2 (continued)

Examples	Properties of transparent coloring composition (I)	
	Transmittance (B)	
	460 nm (%)	610 nm (%)
Experiment 1	10.8	0.9
Experiment 2	66.4	1.5
Experiment 3	12.2	0.8
Experiment 4	66.2	1.6
Experiment 5 (Green)	---	---
Experiment 5 (Red)	---	---
Experiment 5 (Blue)	67.7	1.3

Table 2 (continued)

Examples	Properties of transparent coloring composition (I)		
	Specific absorptivity (based on weight)		
	550 nm ϵ_w (-)	650 nm ϵ_w (-)	610 nm ϵ_w (-)
Experiment 1	---	---	1.45
Experiment 2	---	---	1.42
Experiment 3	---	---	1.49
Experiment 4	---	---	1.70
Experiment 5 (Green)	---	1.72	---
Experiment 5 (Red)	1.58	---	---
Experiment 5 (Blue)	---	---	1.66

Remarks

As seen from the above Tables, the dispersion average particle diameter (Dd_{50}) and the dispersion maximum particle diameter (Dd_{99}) of Experiments 1 to 5 are not less than 338 nm and not less than 1166 nm, respectively, which are respectively out of the scope of our invention.

As a result, the transmittance values at wavelengths of 620 nm of the red-based transparent coloring composition and at wavelengths of 650 nm of the green-based transparent coloring composition of Experiments 5 are 3.1% and 1.5%, respectively, which are inferior to those of Examples of our invention (as seen from the Table 11 of our specification, the transmittance values at wavelengths of 620 nm and 650 nm are less than 1%).

In addition, the transmittance values at wavelengths of 460 nm of the blue-based transparent coloring composition of Experiments 1 and 3 are 10.8% and 12.2%, respectively, which are out of the scope of our invention. Also, the transmittance values at wavelengths of 610 nm of the blue-based transparent coloring composition of Experiments 2, 4 and 5 are 1.5%, 1.6% and 1.3%, respectively, which are inferior to those of Examples of our invention (as seen from the Table 11 of our specification, the transmittance values at wavelengths of 610 nm are less than 1%).

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: May 18, 2006

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